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COVER: Detail of the early Middle Horizon tapestry fragment in William J Conklin's article "Peruvian Textile Fragment from the Beginning of the Middle Horizon". Photograph by Allen C. Marceron.

DRAWINGS by: William J Conklin for "Peruvian Textile Fragment from the Beginning of the Middle Horizon"; Sally Huddles for "Symbolic Scenes in Javanese Batik"; Milton Sonday for "A Type of Mughal Sash".

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PRINCIPLES OF TEXTILE CONSERVATION SCIENCE

NO. XVI

THE USE AND CONTROL OF REDUCING AGENTS AND "STRIPPERS"

James W. Rice

Reducing agents have two principal functions in textile conservation. First, as has been mentioned in our offering on oxidation and bleaching, we have told how they protect from oxidation and control bleaching. Second, we have touched on their decolorizing effect for particular stains.

Out of more than fourteen commonly used reducing agents for textiles that are compounds of sulfur in one form or another, the sulfites or substances formed from sulfur dioxide (SO_2) are probably the most popular and the least expensive. These are natural products resulting from the burning of sulfur, thus $S + O_2 \rightarrow SO_2 \uparrow$ sulfur dioxide (sulfur fumes). As long as this gas is perfectly dry, it has no appreciable effect on dry textiles or fibers. However, when the gas encounters moisture, it reacts immediately to form sulfurous acid (H_2SO_3), thus $SO_2 + H_2O \rightarrow H_2SO_3$. This acid in turn is oxygen hungry and if a textle or fiber surface happens to be damp, the sulfurous acid is produced in place. In turn, the acid will endeavor to take up oxygen from the fiber substances. In doing so, the fibers become reduced and the sulfurous acid is oxidized to sulfuric acid, H_2SO_4, a strong and stable cellulose affecting substance. This is the secret of the "Stoving Process" for decolorizing wool in the early stages of processing. It also destroys vegetable woody matters entangled in the fleeces. Since the wool is not damaged by the acid to any appreciable amount at this stage, the acid may be removed by rinsing and neutralization and no harm is done to the fiber.

Sulfur dioxide gas occurs in appreciable concentrations in most coal and oil smokes and in automobile fumes. As such, through the same sequence of chemical events described under "stoving", the atmospheric sulfurous fumes attack cotton, linen, and rayon curtains that may be accidentally exposed to rain, and eventually develop into the very strong damaging sulfuric acid. This results in weakened and rotted cellulosic materials and is one of the reasons why cotton buntings and flags are short-lived when exposed outdoors.

Nylon is dissolved by sulfuric acid at moderate concentrations. Failure of nylon stockings and cordage may be blamed on the theory just explained.

The chemical shorthand expressions for the last two developments are as follows:

$$SO_2 + H_2O \rightarrow H_2SO_3 \text{ (in wet air)}$$

$$2\,H_2SO_3 + O_2 \text{ (air)} \rightarrow H_2SO_4$$

CONTROL OF OXIDATION DURING WETCLEANING

Laundry practice in the past has occasionally demanded use of reducing agents or antichlors after bleaching with the chlorine bleaches because of a firm attraction of the cellulose fibers towards sodium hypochlorite ($NaOCl$). For this job the principal chemicals used have been sodium bisulfite and oxalic acid. Both are mild reducing agents, are acidic and thus sours also.

The sodium bisulfite ($NaHSO_3$) is supposed to produce, when dissolved in water, sodium sulfite (Na_2SO_3) and sulfurous acid (H_2SO_3) which we have already encountered. For example:

$$2\,NaHSO_3 \xrightarrow[\text{in water}]{} Na_2SO_3 + H_2SO_3. \text{ (Note 1)}$$

According to our previously explained theory, the sulfurous acid (H_2SO_3) is the active oxygen acceptor and in that event attacks and destroys the NaOCl. Thus: $H_2SO_3 + NaOCl \rightarrow H_2SO_4 + NaCl$. In this case the final result is quite acid so, unless the wash solution was alkaline to begin with, as would be probable, the acid might cause tendering to cellulosic fibers. It would not affect wool fibers, however.

When used as an antichlor as explained above, a maximum concentration of about one-fourth percent of the $NaHSO_3$ or preferably less based on the total weight of the reducing bath is recommended. This bath should be hot, at least 140° F. or higher.

Oxalic acid, $H_2C_2O_4$, or HOOCCOOH or $(COOH)_2$, a moderately strong organic acid which is not one of the sulfur compounds, has been in the past a widely used laundry sour and antichlor. It is expected to react with certain oxygen bearing compounds to produce carbon dioxide and water according to the equation, $(COOH)_2 + O_2 \rightarrow H_2O + 2\,CO_2$.

Oxalic acid may be purchased at chemical supply houses, drugstores and cleaning supply firms as nearly pure crystals. Use concentration will vary from 0.2% by weight as an antichlor up to 500% at 190° F. for marble cleaning. Put on rubber gloves in working with it at high concentrations. It is poisonous, so do not swallow it.

Potassium binoxalate, also toxic, KHC_2O_4 or KOOCCOOH is an acid salt of oxalic acid. It has been substituted therefor in European laundry practice because it is supposed to be less likely to cause tendering than the acid.

Sodium hydrosulfite, $Na_2S_2O_4$, another sulfur bearing reducing agent is much more active than those that have been named before. It is widely employed in the cleaning and textile industries as a stain or dye remover where it is known as "stripper."

In vat dyeing, stripper reduces the insoluble dye substance to the leuco state which is soluble in an alkaline solution. When applied to cotton and allowed to oxidize, the original color returns as a washing and ageing fast dye job.

For removal of general stains some but not all colors can be removed by soaking the textile in a 120°-140° 2% hydrosulfite bath for one-half to one hour.[2] If the goods are dyed with other colors, these must be tested for resistance to the stripper or protected by applying a water resistant shield such as wax or a dry solvent removable adhesive. In the main, however, an experienced conservator may employ stripper profitably for many stain removal problems.

Hydrogen sulfide, H_2S, a vile smelling and poisonous gas, is one of the bi-products of the reducing action of the sodium hydrosulfite molecule and is a powerful reducer in its own right. It will attack many metals and produce sulfides which in turn result in black deposits on fabrics in contact. These are especially noticeable on tin weighted silks, metallic threads, buttons and other ornaments. For this reason also one should avoid metal basins and tanks and remove all metal objects from the artifact before treatment.

A little acetic acid, up to about ½% of the bath, will speed up the action of the hydrosulfite stripper so that it may produce results at temperatures around 100° F. Addition of a small amount of alkali will slow the reducing action but will require a much longer time.

This is one way of treating weighted fabrics. The black stain is sometimes removed with hydrogen peroxide plus ammonia.

Sodium hydrosulfite is marketed in brown bottles as a granular powder. On exposure to the air it rapidly hardens and is difficult to remove. Keep the bottle tightly closed. It may be purchased from dyers' and cleaners' supply houses under at least twenty different trade names, but it is all the same chemical.

Formaldehyde sulfoxalate, having a formidable formula $NaHSO_2.CH_2O.\ 2\ H_2O$, is sometimes substituted for hydrosulfite strippers for jobs requiring drastic reduction such as stripping sun-faded garments before redyeing. Wool so treated loses strength but not as much as if the decolorizing is done by oxidation. "Formaldehyde stripper", as it is known to some professional cleaners and dyers, responds to the same acid-alkali and temperature controls as hydrosulfite stripper.

For identification, it is a bluish grey powder and can be purchased from cleaners' and dyers' suppliers.

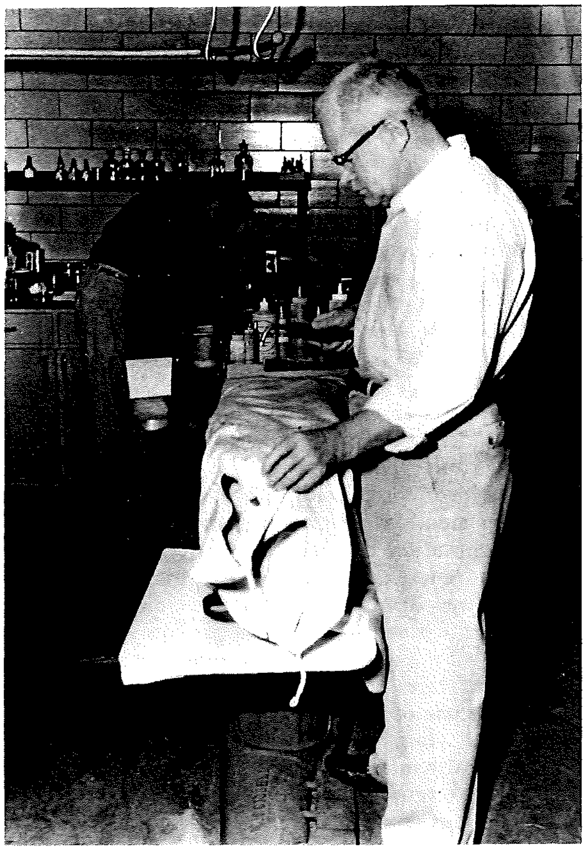

Fig. 1 *Steam-air-vacuum equipment. Courtesy of National Institute of Dry Cleaning.*

THE TITANIUM STRIPPERS

There are two titanium compounds that are widely used by professional cleaners for spot and dye removal by reduction. These are titanous chloride, $TiCl_3$ and titanous sulfate, $Ti_2(SO_4)_3$ both of which are purple liquids and are interesting because they do not contain sulfur. They are excellent organic stain removers and will remove some dye and vegetable stains that will not respond to hydrosulfite stripper. It is also true that the latter may reduce some stains that titanium strippers do not.

In doing their job of lowering the oxidation potential of the coloring substance, the titanium strippers change in valence from Ti^{+++} (three) to Ti^{++++} (four), which is the oxidation state of titanium dioxide TiO_2, an exceedingly useful modern white pigment. This is a stable compound and has no reducing properties. It should not be confused with the titanous liquids.

Our titanous strippers, depending on the problem, may be applied concentrated as they come in the bottle to stains that appear to resist reducing. In this case, they will work faster if heated to boil ing before applying or if heated by steam jet when cold. This latter is a favorite method of application by professional spotters when sophisticated steam-air-vacuum equipment is available. (See Figure 1).

For large discolored areas, titanium strippers may be diluted in proportions of one or two ounces of the liquid per gallon of water. This may do a job at 100° F. or below overnight. At more elevated temperatures (120° to 140° F.) the rate of the reaction doubles every eighteen degrees. In this case, the progress should be kept under observation at reasonable time intervals to avoid over treating. This technique may be used also for bath reduction with sodium hydrosulfite.

In fact, incidents of alternating the application of the two types of strippers have been published [2] but, in this case, thorough rinsing between treatments is necessary to avoid yellow deposits of titanium sulfide, TiS_2.

Sources for procurement of the titanium strippers may be found at local dealers in drycleaning and laundry supplies.

Hydrofluoric acid H_2F_2, or rust remover, has been mentioned before in our Principles of Textile Conservation Science No. XIII. It is considered to be a reducing agent because of the effect of the acid hydrogen ion H^+. In addition to its reducing action, hydrofluoric acid is probably a sequestering agent for ferrous iron, and other metals in their reduced state. Examples of this action may be seen in the use of dilute hydrofluoric acid to remove the yellow stains produced when titanium strippers come in contact with sodium hydrosulfite. It is also used to remove black stains that form when ammonia is added to the titanium stripper scene.[3]

Thiourea, $NH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}NH_2$, when acidified is a reducing agent used for cleaning gold and silver threads and braid. The author has used several trade-named liquids of this general type successfully for brightening insignia on historic military uniforms and on specimens of gold and silver fabrics. In these, where the insignia could be dipped in the solution and then rinsed in distilled water, the results were excellent. When the fluid was brushed on and then rinsed and dried, the results were satisfactory but not quite so bright. Some of the products tried for this were "Silver Dip", a product made by J. Goddard and Sons, Ltd., Leicester, England; "Braid-Nu" by Arlenge Laboratories, New York City 10007; "Parade Dress", EZ-EST Products Co., Oakland, California 94607, and "Instant Dip" by Lewell Industries, 23 Popham Road, Scarsdale, New York.[4] None of these should be used on iron or stainless steel.

NOTES

[1] G. P. Fulton, *Applied Science for Drycleaners,* National Institute of Cleaning and Dyeing, Silver Spring, Maryland, 1951. Pages 229 and 235.

[2] Norbert J. Berg, *Wetcleaning,* National Association of Dyers and Cleaners of the United States and Canada. Silver Spring, Maryland. Page 167.

[3] See Note 1.

[4] Louisa Bellinger, *Cleaning of Textiles,* International Institute for Conservation of Historic and Artistic Works, 1964 Delft Conference on Conservation of Textiles. Collected reprints, 2nd edition, 1965.